Twist disclination loops and their dissociation in polymer crystals

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Geometric and energetic properties of twist disclination loops in polymer crystals are analysed theoretically. The phenomenon of dissociation of a perfect twist loop into several partial loops joined by stacking faults is described quantitatively. The strain energy associated with a rectangular twist loop and the energy of elastic interaction between two disclination loops in a polymer crystal are calculated in an analytical form. It is shown that the dissociation of the perfect twist loop in a polyethylene crystal leads to a significant decrease in the total defect energy. A continuum disclination model of a kink defect is proposed and applied to the theoretical calculations of the energetics of kinks in polyethylene. The results of disclination theory are compared with the data obtained in computer simulations of defects in polyethylene crystals. From this comparison the core sizes of twist and wedge disclination loops in polyethylene are estimated.

(Keywords: crystals; defects; disclination theory; dissociation and energies of disclinations)

INTRODUCTION

It is well known that disclinations (line defects of rotation type) are imperfections appropriate to polymers. Disclinations exist on various scales and serve as elementary carriers of plastic rotations both in the low-molecular crystals and in the polymers. However, peculiarities of a molecular structure lead to the formation of the disclination defects of specific type in polymers.

Owing to the fact that the interaction forces between macromolecules are considerably weaker than the interatomic bonds within chain molecules the particular scale level appears in polymer systems. This level is characterized by the dimensions of macromolecule cross-sections which can be considerably larger than the minimum scale prescribed by the interatomic distances. In such a situation 'molecular' disclinations can be created which are inherent only in high-molecular compounds. These defects of microscopic dimensions were first described by Li and Gilman[1]. Strictly speaking, they are disclination loops enveloping a single molecular chain or several neighbouring chains. Disclination loops are usually subdivided into wedge and twist loops which provide plastic bend and twist of macromolecules.

The ideas about molecular disclination defects in polymers were further developed by Vladimirov and Pertsev[2]. It was shown that two different kinds of disclination loops exist. These defects, distinguished by their properties, were termed 'internal' and 'external' disclination loops[2]. An internal loop has the plastic rotation surface localized in the corresponding cross-section of macromolecule. Defects of this kind form only in the systems of flexible chain molecules because their nucleation requires internal rotation around the backbone bonds (*Figure 1*). The set of values available for the internal loop strength is determined by the positions of minima of the chain internal rotation potential. It should be noted that internal disclination loops can occur both in solid polymers and in polymer melts and solutions.

In case of an external loop, the surface of plastic rotations coincides with the lateral surface of a part of the macromolecule (*Figure 2*). Accordingly, strong intermolecular forces are necessary in a polymer system to bring about the appearance of external loops. These defects are inherent in solid polymers, whereas in polymer solutions, for example, they become unstable. In a polymer crystal the strengths of external loops are defined by the shape of intermolecular potential related to the rotation of a macromolecule as a stiff rod (see next section).

External and internal disclinations differ from each other not only by geometric parameters but also by their energies and mobilities[2].

The disclination approach makes it possible to work out continuum models for the structural imperfections of rotation nature in solid polymers, i.e. conformational defects (kinks, crankshaft configurations, Reneker defects) and chain folds[1–3]. A number of these defects were studied by means of computer modelling in the simple case of polyethylene crystals[4–9]. Using the results obtained and applying the methods of disclination theory it is possible to describe quantitatively other defects in polyethylene and to proceed to the calculation of the defect energies in polymers with complicated atomic structure[2].

This paper is devoted mainly to the analysis of external twist loop properties in polymer crystals. The first section describes theoretically the process of dissociation of a perfect twist loop into several partial loops joined by stacking faults. This effect is similar to the dissociation of dislocations and dispirations in crystals[10,11]. Theoretical calculations are compared with the computer modelling

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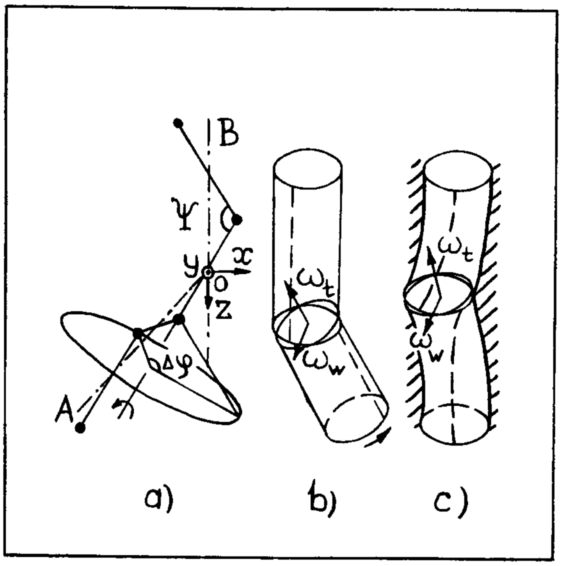

Figure 1 Geometry of rotation of skeletal bond in a polymer chain (a) and formation of internal twist and wedge disclination loops in an isolated chain (b) and in a macromolecule incorporated into a solid polymer (c). Here $\Delta\phi$ denotes the variation of internal rotation angle (torsional angle) and Ψ is the valence angle of the chain. $\boldsymbol{\omega}_w$ and $\boldsymbol{\omega}_t$ are the Frank vectors of wedge and twist loops

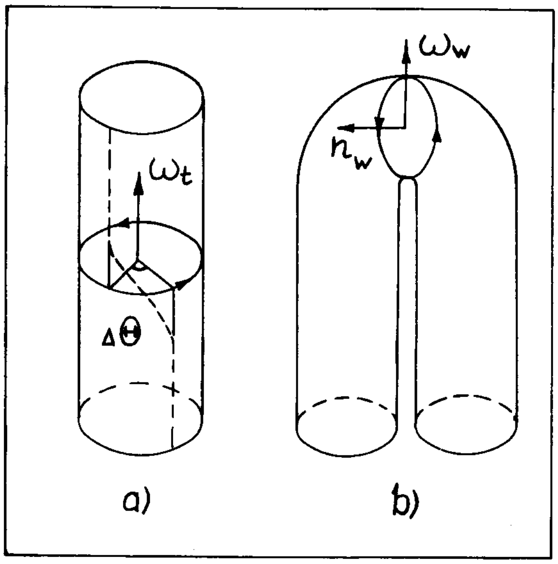

Figure 2 External disclination loops in a polymer crystal. (a) Twist disclination loop of strength $\omega_t = \Delta\theta$. (b) Wedge loop of strength 180° which is the characteristic element of a chain folded lamellar crystal structure

data[7] and on this basis the core dimension in the [001] plane of polyethylene crystal is estimated for a twist disclination. The influence of dissociation process on the self-energy of the twist loop is considered (see second section). In the third section a disclination description is given to the process of kink formation in a polymer crystal and the core dimension in the [001] plane of polyethylene crystal is calculated for a wedge disclination loop.

The motions of external twist disclination loops provide reorientation of the molecular electric dipoles which occurs in the chains of polar polymers under the influence of applied electric fields. Disclination mechanisms operate, for instance, in the processes of polarization switching in the β-phase of ferroelectric polyvinylidene fluoride and in the α–δ phase transition in this polymer (see ref. 12 and references therein). These facts support the importance of studying properties of twist disclination loops.

THEORY

Geometry of dissociation of twist disclination loops

In a polymer single crystal the Frank vector $\boldsymbol{\omega}_t$ of external twist loop and the unit normal $\mathbf{n}_t$ to its location plane are oriented along the chains (see *Figure 2a*). Disclination line usually surrounds only a single macromolecule[7] but it can envelop several neighbouring chains if they are twisted around one common axis. In this paper only the first case is considered.

Mutual twisting of two parts of a macromolecule surrounded by a disclination loop is purely elastic. This twist is realized around the longitudinal chain axis. The strength ω_t of a disclination is equal to the dihedral angle $\Delta\theta$ between the planes of two molecular backbone segments which are located far from the defect (see *Figure 2a*). To provide stability of elastically deformed chain these segments must have definite setting angles θ and $\theta + \Delta\theta$ in a unit cell corresponding to the minimum energy positions of macromolecule in the lattice. Accordingly, allowed values of plastic rotation $\Delta\theta$ are determined by the shape of potential $E_{\mathrm{ER}}(\theta)$ describing the energetics of a perfect chain that rotates around its longitudinal axis in the crystal. The set of allowed ω_t values can be calculated from the expression $\omega_t = \theta_p - \theta_q + 2\pi k$, where k is an integer; θ_p, θ_q ($p, q = 1, 2, \ldots, r$) are the points of $E_{\mathrm{ER}}(\theta)$ minima on the interval $[\theta_1, \theta_1 + 2\pi]$. θ_1 is the crystallographic setting angle of a chain in the perfect lattice.

The external twist loops can be both perfect and partial disclinations[2,7]. The strengths of perfect loops are fixed by the symmetry of polymer macromolecule, namely, $\omega_t = 2\pi k/l$ when macromolecule has l-fold symmetry axis[13]. A partial disclination loop is connected with a cylindrical surface of stacking fault surrounding a chain segment undergoing plastic rotation. The stacking fault energy per unit length of this segment is given by $\gamma(\theta) = E_{\mathrm{ER}}(\theta)/L$ (L is the length of macromolecule).

In a polymer crystal a substantial part of disclination loop self-energy is the energy W_s of elastic strain fields existing in the surrounding lattice. The elastic energy W_s calculated in continuum linear approximation[1] increases in direct proportion to ω_t^2. This result shows that only the twist loops having minimum strengths $\omega_t^{(m)} = \theta_{m+1} - \theta_m$ ($m = 1, 2, \ldots, r$; $\theta_{r+1} = \theta_1 + 2\pi$) are stable in a crystal. Defects with greater strengths ω_t convert into a system of two or more 'elementary' disclination loops. The total Frank vector of such a system is equal to the rotation vector of initial loop.

The most important example of disclination defect transformation is the dissociation of a perfect disclination loop into partial loops joined by a cylindrical zone of stacking faults (see *Figure 3*). These dissociation processes occur only in the polymers where partial disclination loops of strength $\omega_t < 2\pi/l$ can exist. When a perfect external loop dissociates into partials the elastic energy of polymer crystal decreases whereas the excess packing energy associated with stacking faults increases. Therefore, an equilibrium length z^* of the stacking fault zone exists minimizing the total energy of the polymer system.

Consider first the dissociation of perfect twist loop into two partial defects (*Figure 3*). Using disclination theory it is possible to calculate the equilibrium distance z^* between the partial loops. The condition of equilibrium requires the total force acting upon each partial loop to go to zero. This total force includes the force of elastic repulsion f between two disclination loops and the generalized attractive force due to the stacking fault. Accordingly, the distance z^* can be calculated by solving the following equation:

$$f(z) = -\frac{\partial W^{t}_{int}(z)}{\partial z} = \gamma(\theta) \qquad (1)$$

where $W^{t}_{int}(z)$ is the elastic interaction energy between two twist disclination loops lying in the planes $z=0$ and $z=z$. $\gamma(\theta)$ is the stacking fault energy per unit length of the chain segment situated between partial loops and θ is the setting angle of this segment.

The interaction energy W^{t}_{int} was calculated here within the linear anisotropic theory of elasticity for the rectangular disclination loops as developed in the Appendix. This shape of the loop permits us to allow for the 'unequiaxiality' of a molecule cross-section[2]. This is in contrast to previous work[1] that studied circular loops. (The shape and the dimensions of a loop surrounding a single chain are determined by the geometry of the mean cross-section of macromolecule). In the theory polymer crystal was treated as a transversely isotropic elastic continuum. This approximation takes account of the high elastic anisotropy inherent in the polymer crystals[14,15].

Substituting in equation (1) the analytic expression for the force $f(z)$, derived by differentiation of equation (A2) (see Appendix), we can solve equation (1) numerically and estimate the distance z^*. Numerical computations were carried out for the case of a polyethylene single crystal containing perfect twist loop with a strength of 360° which dissociates into two partial loops of equal strength $\omega^{(1)}_{t} = \omega^{(2)}_{t} = 180°$. Such a disclination defect was studied earlier by means of computer modelling[7]. In the calculations the value of $\gamma(\theta_1 + 180°) = 2.8 \times 10^{-11}\ \mathrm{J\,m^{-1}}$ was used for the stacking fault energy in accordance with the results of McCullough[16] who computed the $E_{ER}(\theta)$ potential for macromolecules in polyethylene crystals. The other parameters used (the dimensions $2d$ and $2h$ of the loops and the crystal elastic constants c_{ij}) were chosen as described in the Appendix.

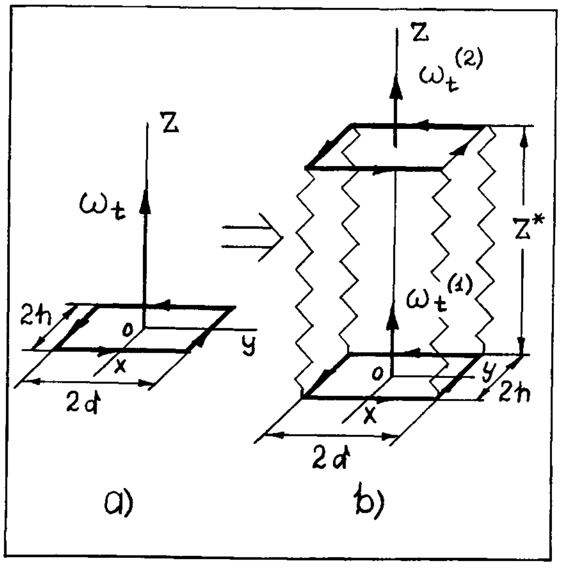

Figure 3 Dissociation of a twist perfect disclination loop having Frank vector $\boldsymbol{\omega}_t$ into two partial loops with rotation vectors $\boldsymbol{\omega}^{(1)}_{t}$ and $\boldsymbol{\omega}^{(2)}_{t}$. In the dissociation process the condition $\boldsymbol{\omega}_t = \boldsymbol{\omega}^{(1)}_{t} + \boldsymbol{\omega}^{(2)}_{t}$ holds. Wavy lines designate the stacking fault zones. $2d$ and $2h$ denote the disclination loop sizes. Axis z of coordinate system (x, y, z) is oriented along the chain axis

The equilibrium distance between two partial loops, z^*, calculated from equation (1) with the aid of a computer, was found to be $z^* = 4.5$ Å. From Figure 14a of ref. 7 we can extract the estimate $z^* \approx 7.5$ Å of the dissociation extent given by the computer modelling. It should be noted that in disclination calculations the approximation $\omega^{(1)}_{t}, \omega^{(2)}_{t} \ll 1$ was used and the nonlinear contributions were omitted which are significant when $\omega^{(1)}_{t} = \omega^{(2)}_{t} = 180°$. Thus, the agreement between disclination theory and computer modelling results can be regarded as satisfactory.

Depending on the polymer structure, the perfect disclination loop can dissociate also into three, four and more partial defects. For instance, the polypropylene molecule has a screw axis of three-fold symmetry[17]. Therefore, in a polypropylene crystal the perfect twist loop of strength 360° must dissociate into three partial loops. In turn, the polyethylene energetic potential $E_{ER}(\theta)$ is characterized by three intermediate minima on the interval $(\theta_1, \theta_1 + 360°)$ corresponding to chain rotations of 68°, 170° and 260° with respect to the standard orientation $\theta_1 = 48°$ (ref. 16). In this situation, for a perfect twist loop of strength 360° to be energetically favourable it is necessary to dissociate into four partial loops joined by three stacking fault strips (see *Figure 4*). This supposition is partly confirmed by the computer modelling[6] of a partial twist loop with strength 180° in polyethylene showing that this defect consists of two partial loops, each of strength 90°.

Hence, it seems worthwhile to study the dissociation geometry in the case when four partial loops form in polyethylene. Let us assume for simplicity that these loops have equal strengths ($\omega^{(1)}_{t} = \omega^{(2)}_{t} = \omega^{(3)}_{t} = \omega^{(4)}_{t} = 90°$) and that the two lateral stacking fault strips (see *Figure 4*) have equal energies per unit length: $\gamma(\theta_1 + 90°) = \gamma(\theta_1 + 270°)$. Then the disclination configuration will be symmetric. To specify its geometry it is sufficient to consider the conditions of equilibrium of forces only for the two loops having the Frank vectors $\boldsymbol{\omega}^{(1)}_{t}$ and $\boldsymbol{\omega}^{(2)}_{t}$ (see *Figure 4*). Accordingly, the equilibrium distances z^*_1 and z^*_2 between adjacent twist loops can be calculated by solving the following system of simultaneous equations:

$$\frac{\partial W^{t}_{int}(z_2)}{\partial z_2} + \frac{\partial W^{t}_{int}(z_1+z_2)}{\partial (z_1+z_2)} + \frac{\partial W^{t}_{int}(z_1+2z_2)}{\partial (z_1+2z_2)} + \gamma(\theta_1 + 90°) = 0$$

$$\frac{\partial W^{t}_{int}(z_1)}{\partial z_1} + \frac{\partial W^{t}_{int}(z_1+z_2)}{\partial (z_1+z_2)} - \frac{\partial W^{t}_{int}(z_2)}{\partial z_2} + \gamma(\theta_1 + 180°) \qquad (2)$$

$$-\gamma(\theta_1 + 90°) = 0$$

where $W^{t}_{int}(z)$ is the interaction energy given by equation (A2) (see Appendix) with $\omega^{(1)}_{t} = \omega^{(2)}_{t} = 90°$. The value of $\gamma(\theta_1 + 90°)$ was determined as an arithmetic mean of the exact stacking fault energies $\gamma(\theta_1 + 68° \simeq 2.1 \times 10^{-11}\ \mathrm{J\,m^{-1}}$ and $\gamma(\theta_1 + 260°) = 3.1 \times 10^{-11}\ \mathrm{J\,m^{-1}}$ calculated by McCullough[16]. Numerical computations

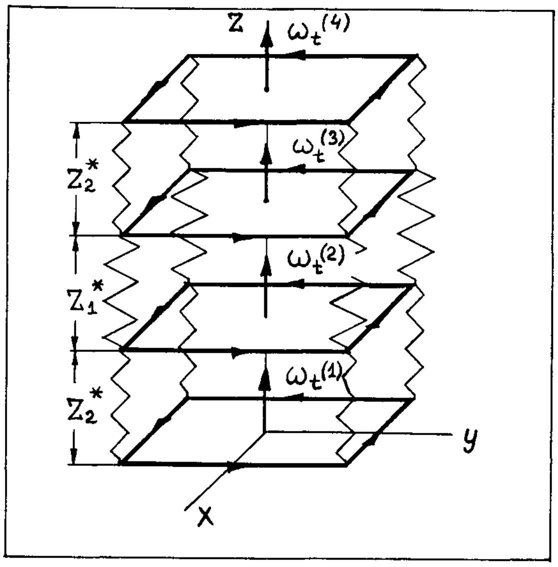

Figure 4 Schematic illustration of the dissociation of the perfect twist loop with strength 360° into four partial loops having strengths $\omega_t^{(1)} \approx \omega_t^{(2)} \approx \omega_t^{(3)} \approx \omega_t^{(4)} \approx 90°$ in polyethylene. z_1^* and z_2^* are the equilibrium distances between adjacent disclinations

Table 1 Geometric parameters and energies of twist disclination systems with total strength 2π in polyethylene

Number of disclination loops in chain	Total length of disclination on system, (Å)	Total energy of disclination system, U (eV)	Energetic effect of dissociation, $U_I/U_{II,IV}$
1	–	1.49	–
2	4.5	0.83	1.8
4	9.8	0.56	2.6

based on equation (2) gave the values of $z_1^* \approx 3.2$ Å and $z_2^* \approx 3.3$ Å for the distances between partial loops in the disclination defect. Thus, the total length of this defect is considerably greater than that of the defect dissociated into two partial loops (see *Table 1*).

In general, when a perfect twist loop dissociates into N partial loops joined by $(N-1)$ stacking fault strips, we have to solve a system of $(N-1)$ simultaneous equations similar to equation (2) to determine the configuration of this ensemble.

Energies of twist disclination loops in polyethylene crystals

Effect of dissociation processes. In the theory of dislocations and disclinations the total energy U of a linear defect is usually represented[1,10] as a sum of the elastic energy W_s and the core energy E_c. The first term is the excess energy of deformed lattice in that part of a crystal where strains are sufficiently small so that the energy density can be calculated in the framework of linear elasticity theory. The second term is the extra energy of a cylindrical region coaxial with dislocation or disclination line where the interatomic forces undergo strong nonlinear changes (the core region). The precise values of the core dimensions and the energy E_c can be determined only by detailed atomistic calculations.

For a twist disclination loop, the elastic energy W_s^t is given by the analytic equation (A3) (see Appendix) obtained here within the linear anisotropic theory of elasticity (see the Appendix). Equation (A3) shows that the value of W_s^t depends on the disclination core dimension $2r_t$ measured in the loop plane. Hence, the core energy contribution E_c can be taken into account formally if the elastic term W_s^t is increased to a certain extent by substituting an effective core dimension into equation (A3). In this procedure r_t is used as an adjustable parameter of the disclination theory which is determined from the comparison between theoretical results and the computer simulation data for the defect total energy U.

Let us apply the above method to the evaluation of the effective core dimension $2r_t$ for an external twist loop lying in the [001] plane of polyethylene crystal. Computer modelling[7] of the twist defect with total strength 360° in polyethylene showed that it has an energy of 0.83 eV in the state when this defect is equivalent to the equilibrium disclination system containing two partial twist loops of equal strength 180° (see *Figure 3*). The total energy U_{II} of this disclination system can be written as

$$U_{II} = 2W_s^t + W_{int}^t(z^*) + \gamma(\theta_1 + 180°)z^* \quad (3)$$

where the twist loop self-energy W_s^t is given by equation (A3), W_{int}^t is the elastic interaction energy between two disclination loops defined by equation (A2) and z^* denotes the equilibrium separation of disclination loops calculated in the previous section. Using equation (3) and taking $U_{II} = 0.83$ eV we obtain transcendental equation in the unknown parameter r_t characterizing the twist loop of strength 180°. The effective core dimension, calculated numerically from this equation, was found to be $2r_t = 0.66$ Å. (Due to the strong elastic anisotropy of polyethylene crystals the disclination core must be modelled by a cylindrical region having an elliptical cross-section[18]. The dimension r_t is the ellipse semiaxis in the [001] plane of polyethylene crystal.) It should be noted that the parameter r_t obtained has the same order of magnitude as the core radii of dislocations in nonmetallic crystals[10].

From equation (3) it can be also deduced that the total self-energy U of an isolated twist loop of strength 180° in polyethylene is about 0.37 eV. (The energy of the stacking fault zone connected with this partial loop is not included in U.) The core energy E_c of the disclination loop according to Li and Gilman[1] should be of the order of 0.1 eV. Thus, the elastic energy is the main part of the total energy of disclination loop.

The above quantitative results provide a basis for theoretical study of the energetics of complicated disclination configurations in polyethylene that are difficult to investigate by computer simulations. It should be mentioned that, in principle, the effective core dimension r_t could depend on the other parameters of the disclination loop (on its strength, for example). However, in the calculations of disclination energies these dependences can be ignored in view of the fact that the elastic energy W_s^t weakly depends on the r_t value ($W_s^t \sim \ln r_t$).

Using the calculated value of $2r_t = 0.66$ Å we can analyse the effect of dissociation on the energy of a twist loop with strength 2π in polyethylene. When this perfect loop dissociates into four partial loops (see *Figure 4*) the total energy U_{IV} of disclination system in equilibrium state is given by

$$\begin{aligned} U_{IV} = {} & 4W_s^t + W_{int}^t(z_1^*) + 2W_{int}^t(z_2^*) + 2W_{int}^t(z_1^* + z_2^*) \\ & + W_{int}^t(z_1^* + 2z_2^*) + 2\gamma(\theta_1 + 90°)z_2^* + \gamma(\theta_1 + 180°)z_1^* \end{aligned} \quad (4)$$

where W_s^t and W_{int}^t are the self- and interaction energies of the loops having the strength $\pi/2$; z_1^* and z_2^* denote the equilibrium distances between disclinations calculated in the previous section. The energy U_{IV} computed on the basis of equation (4) is listed in *Table 1* together with the energy U_I of an undissociated perfect twist loop and the energy U_{II} of a defect involving two partial loops with strength 180° (see *Figure 3*). Comparison of the values listed in *Table 1* shows that the defect energy strongly depends on the degree of dissociation. Thus, the effects of dissociation processes are to be taken into account when analysing the energies and the probability of nucleation of perfect disclinations in polymer crystals.

Disclination model of kink defect

Theoretical description of kink energetics in polyethylene. One of the typical defects occurring in polymer crystals is a conformational defect termed 'kink' that has received considerable attention[4,17,19–21]. To form a kink it is sufficient to incorporate the conformational sequence ... tttgtg′ttt ... into a crystal by straining two planar zig-zag stems so they lie along the same (001) axis of the lattice[19] (see *Figure 5a*). In the process of kink creation the defect chain undergoes a double plastic bend realized by an internal rotation (the middle bond *t* in *Figure 5a* is rotated by an angle $\Delta\phi$). In addition, the three bond segment inside the kink rotates around its longitudinal axis. Accordingly, the continuum model of kink defect includes two pairs of twist and wedge internal disclination loops opposite in sign (see *Figure 5b*). Previously, it was considered that the kink disclination model consists of wedge loops only[1].

It should be noted that the kink causes a crystallographic mismatch of the defect chain along the (001) axis as a result of the shortening of the kinked segment[4]. Boyd[4] has shown that this lattice mismatch can be treated by continuum elasticity and that its magnitude reduces to zero at large distances from the defect (at distances of about 50 Å). Hence, the disclination model proposed is also suitable to account for the effect of chain shortening. With the disclination approach this shortening appears as a result of the double plastic bend created by two wedge loops.

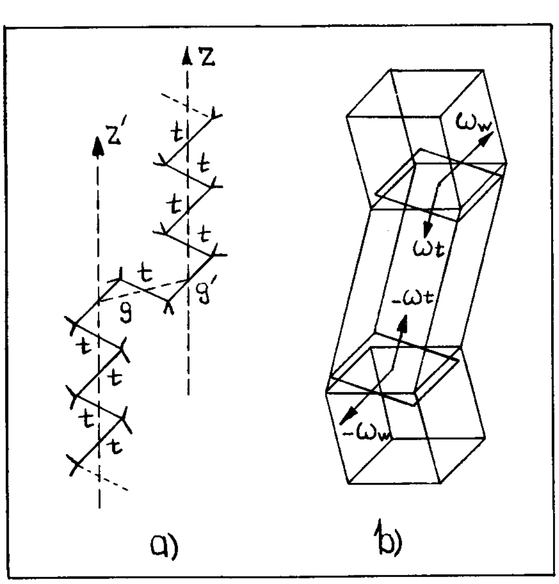

Figure 5 **a**, Schematic illustration of a macromolecule containing conformational kink defect. **b**, Continuum disclination model of a kink in a polymer crystal

For internal molecular disclinations, the Frank vectors $\boldsymbol{\omega}_w$ and $\boldsymbol{\omega}_t$ of wedge and twist loops and the orientations of the unit vectors $\mathbf{n}_w$ and $\mathbf{n}_t$ perpendicular to their location planes are determined by the skeletal bond torsional angle $\Delta\phi$ measured relative to all *trans* conformations (see *Figure 1a*). Vladimirov and Pertsev[2] derived nonlinear equations which allow the calculation of these vector parameters of internal loops in the whole range of $\Delta\phi$ variation ($0° \leqslant \Delta\phi \leqslant 360°$). If the twist loop is introduced into a chain after the wedge one then these equations can be written as

$$\boldsymbol{\omega}_w = \frac{\arccos(\sin^2\Psi/2+\cos^2\Psi/2\cos\Delta\phi)[\sin\Delta\phi\mathbf{i}+\sin\Psi/2(1-\cos\Delta\phi)\mathbf{j}]}{[\sin^2\Delta\phi+\sin^2\Psi/2(1-\cos\Delta\phi)^2]^{1/2}} \tag{5}$$

$$\boldsymbol{\omega}_t = \arccos\left[\cos\Delta\phi+\frac{\cos^2\Psi/2\sin^2\Delta\phi(1-\cos\Delta\phi)}{\sin^2\Delta\phi+\sin^2\Psi/2(1-\cos\Delta\phi)^2}\right]\mathbf{n}_t \tag{6}$$

$$\mathbf{n}_w = \frac{1/2\sin\Psi(\cos\Delta\phi-1)\mathbf{i}+\cos\psi/2\sin\Delta\phi\mathbf{j}+(1+\sin^2\Psi/2+\cos^2\Psi/2\cos\Delta\phi)\mathbf{k}}{[2(1+\sin^2\Psi/2+\cos^2\Psi/2\cos\Delta\phi)]^{1/2}} \tag{7}$$

$$\mathbf{n}_t = 1/2\sin\Psi(\cos\Delta\phi-1)\mathbf{i}+\cos\Psi/2\sin\Delta\phi\mathbf{j} + (\sin^2\Psi/2+\cos^2\Psi/2\cos\Delta\phi)\mathbf{k} \tag{8}$$

where **i**, **j** and **k** are the unit vectors of the rectangular Cartesian reference frame in *Figure 1a*; Ψ denotes the valence angle of the chain. Maximum values of the disclination strengths ω_w and ω_t can be achieved when $\Delta\phi = 180°$ ($\omega_w^{max} = 180° - \Psi$, $\omega_t^{max} = 180°$). The strengths of stable internal loops are calculated by substituting into equations (5)–(6) the values $\Delta\phi_i$ ($i = 1, 2, 3, \ldots k$) of torsional angle corresponding to the conformational transitions.

Consider in detail the disclination model of a kink in polyethylene. If the amount of internal rotation $\Delta\phi$ in the defect chain equals 180° then the three bond segment inside the kink falls into the minimum position of interchain potential $E_{ER}(\theta)$. Hence, this segment undergoes plastic rotation of $\Delta\theta = 180°$ with respect to surrounding lattice and in this situation two additional (external) twist loops having strengths 180° and −180° appear in the crystal. The contour of the external loop coincides with that of internal twist loop described above but they are opposite in sign. Accordingly, in the kink with $\Delta\phi = 180°$ the external and internal twist loops elastic fields exactly compensate each other. The resulting disclination model of such a kink consists of two wedge loops only. For all other kink configurations ($\Delta\phi \neq 180°$), the total strength ω_t^{Σ} of the twist disclination loops is given by equation (6) provided $\Delta\phi \leqslant \Delta\phi_c$ or by the formula $\omega_t^{\Sigma} = 180° - \omega_t$ provided $180° > \Delta\phi > \Delta\phi_c$. (Here $\Delta\phi_c$ is an angle whose substitution into equation (6) gives the value of $\omega_t = 90°$.)

According to the disclination model proposed the total energy U_k of a kink defect can be expressed as follows:

$$U_k = 2W_s^w + 2W_s^t + W_{int}^w + W_{int}^t + E_{IR} \qquad (9)$$

where W_s^w and W_s^t are the self-energies of the wedge and twist disclination loops, W_{int}^w and W_{int}^t are the elastic interaction energies between the loops of the same kind, $E_{IR}(\Delta\phi)$ denotes the excess intramolecular energy of the isolated kinked macromolecule that results from van der Waals interactions and torsional 'inherent' potentials of the -c-c- bonds. Equation (9) does not contain the energy of elastic interactions between wedge and twist loops because for the disclination configuration discussed here this energy is exactly zero in linear elasticity. (Using linear approximation we neglect in equation (9) the part of energy U_k connected with chain shortening caused by the kink. Results obtained by Boyd[4] show that this contribution is significant but not dominant.) The energies W_s^w and W_{int}^w of rectangular wedge disclination loops in transversely isotropic media were calculated earlier in analytic form[18]. The expression derived for the self-energy W_s^w contains the core dimension $2r_w$ of a wedge loop[18]. In this paper r_w is used as an adjustable parameter of the theory that enables us to take into account the contribution of disclination core energy.

Equation (9) was applied to calculate the theoretical energy curve $U_k(\Delta\phi)$ for the kink creation in polyethylene in order to compare it with that obtained by computer simulations[4]. In the computations the intramolecular potential E_{IR} was assumed to be equal to the doubled torsional potential of a -c-c- bond:

$$E_{IR}(\Delta\phi) = e_0(1 - \cos 3\Delta\phi) + e_1(1 - \cos\Delta\phi) \qquad (10)$$

The same torsional potential parameters e_0 and e_1 as used by Boyd[4] were employed ($e_0 = 0.11$ eV, $e_1 = 0.03$ eV). When calculating the dependences of disclination energies on the angle $\Delta\phi$ only the strengths variations $\omega_w(\Delta\phi)$ and $\omega_t(\Delta\phi)$ were taken into account. The orientations of Frank and unit normal vectors were assumed to be invariable and given by equations (5)–(8) in the limit of $\Delta\phi \rightarrow 0$. The effective core dimension, $2r_w$, measured in the wedge loop plane was determined by fitting the theoretical energy U_k to the computer modelling energy value[4] for a kink with $\Delta\phi = \pi$. This approach guarantees that the computed value of r_w is independent of the estimate obtained earlier for the twist loop core dimension $2r_t$. Calculations based on equations (9)–(10) show that the core dimension $2r_w$ in the [001] plane of polyethylene crystal is about 0.3 Å. Thus, the effective core dimensions of wedge and twist loops are of the same order of magnitude ($2r_t \approx 0.66$ Å).

The theoretical energy curve $U_k(\Delta\phi)$ is shown in *Figure 6* together with the data obtained by computer simulations[4]. It is apparent that our disclination model describes satisfactorily the energetics of a kink in polyethylene. The theoretically predicted kink energy U_k^* (corresponding to the position $\Delta\phi^*$ of the metastable equilibrium) is in good agreement with that of Boyd[4]. The discrepancy between the curves plotted in *Figure 6* is mainly due to the approximations used in mathematics of disclination theory.

Substituting the obtained value of $2r_w = 0.3$ Å into equation (5) of ref. 18 we can calculate also the total self-energy W_s^w of an isolated wedge loop in polyethylene. Computations show that this energy is considerably higher than the self-energy of a twist loop having the same dimensions and strength: $W_s^w / W_s^t \approx 20$.

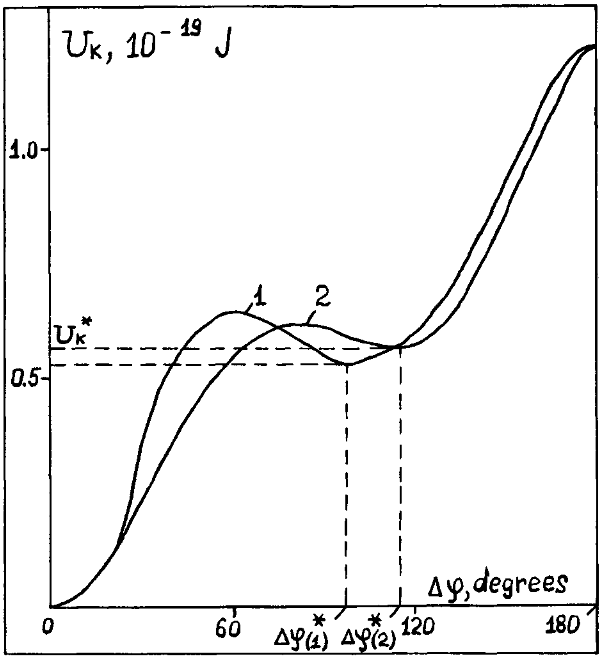

Figure 6 Energetics of a kink defect in a polyethylene crystal. The kink energy U_k is plotted *versus* the skeletal bond torsional angle $\Delta\phi$ measured relative to all *trans* conformation. The curve 1 represents the results of computer simulations performed by Boyd[4]. Curve 2 is the theoretical dependence $U_k(\Delta\phi)$ obtained in this work on the basis of the disclination model

SUMMARY

In this work the disclination theory has been used for the first time for calculating the energetics and the geometry of crystallographic and conformational molecular defects in polymer crystals. The validity of such an approach has been confirmed by the comparison of theoretical results with the data obtained by computer simulations[4,7] of two defects appropriate to polyethylene. From this comparison the sizes of twist and wedge disclination cores in polyethylene crystal have been estimated.

The advantage of disclination modelling is the possibility of obtaining analytical expressions (in continuum approximations) for elastic strain fields and related characteristics of molecular defects in polymers which have any degree of structural complexity. In the investigations of defect energies, disclination theory and computer modelling supplement each other. Such combined calculations make it possible to obtain valuable information about the energetics of various defect ensembles that can occur in polyethylene crystals and to estimate in the first approximation the energies of disclination loops in other crystalline polymers.

Molecular disclinations can multiply, annihilate and move under the influence of external mechanical and electrical fields and with the aid of thermal fluctuations. Accordingly, they can participate in the realization of various physical processes connected with structural changes in polymers. Analysis of the ideas developed in previous studies[4–6,12,20–22] shows that disclination loops must play important roles in the following processes: the thickening of lamellar crystals through annealing (twist loops diffuse being a part of Reneker defects); the disordering of crystals near the melting point (due to increasing density of kinks); the kink band formation in oriented polymers (disclination loops created as a part of slipped kinks); the low-temperature internal friction; the dielectric relaxations in polar polymers (for example, the α-relaxation in polyethylenes containing carbonyl groups); the polarization switching in the β-phase of ferroelectric polyvinylidene fluoride and the α–δ phase transition in this polymer occurring under the influence of an applied electric field.

Thus, applications of the disclination theory to the studies of defects appropriate to crystalline polymers are important for understanding the structure/property relationships in these materials.

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APPENDIX

Consider a rectangular twist disclination loop lying in the isotropic plane $z=0$ of the transversely isotropic medium (see *Figure 3*). The isotropic planes of this medium used as a continuum model of polymer crystals are perpendicular to the chain axes. The disclination Frank vector $\boldsymbol{\omega}_t^{(1)}$ is applied at the geometric centre of rectangular loop contour with sides $2h$ and $2d$. The elastic strain fields associated with the twist loop can be calculated on the basis of the integral expression given by de Wit[23] and the analytic Green's function of a transversely isotropic medium[24]. Using the generalized Hooke law and the strains obtained it is easy to compute the disclination stress tensor $\sigma_{ij}^{(1)}$ $(i,j=x,y,z)$ which is necessary for calculations of disclination energies. In turn, the sought energy $W_{\text{int}}^{\text{t}}$ of interaction between two twist loops can be evaluated by calculating the additional work done in creating the second loop (lying in the $z=z$ plane) in the stress field $\sigma_{ij}^{(1)}$ of the first one. Hence, we can write that

$$W_{\text{int}}^{y}=\int_{(-d)}^{d}\mathrm{d}y\int_{(-h)}^{h}\mathrm{d}x\,\omega_{\text{t}}^{(2)}\left[y\sigma_{xz}^{(1)}(x,y,z)-x\sigma_{yz}^{(1)}(x,y,z)\right]\qquad\text{(A1)}$$

By performing corresponding computations one can obtain the following explicit expression[25] for elastic interaction energy between two twist loops with equal sizes and coaxial Frank vectors $\omega_{\text{t}}^{(1)}$ and $\omega_{\text{t}}^{(2)}$:

$$\begin{aligned}W_{\text{int}}^{\text{t}}=\frac{c_{44}\omega_{\text{t}}^{(1)}\omega_{\text{t}}^{(2)}}{4c_{11}c_{66}}\left(\frac{S}{p}\right)^{3/2}\sum_{l=1}^{3}\Bigg\{&\frac{4F_lp\zeta}{a_l}\arctan\left(\frac{4a_lp}{\zeta R_l}\right)\\&+\frac{(13B_l-7a_l\,F_l)}{9a_l^3}(R_l^{*3}+R_l^{**3}-R_l^3-\zeta^3)\\&+\frac{(5a_lF_l+B_l)}{3a_l^3}\zeta(R_l^{**}+R_l^{*}-R_l-\zeta)\qquad\text{(A2)}\\&+\left[\frac{2(B_l-a_lF_l)}{3a_l^{3/2}}+\frac{2B_lp^2}{a_l^{3/2}}+\frac{(a_lF_l+B_l)}{a_l^{5/2}}\zeta^2\right]\\&\times\ln\left|\frac{(R_l^{*}-2\sqrt{a_l})(R_l+2\sqrt{a_l})}{(R_l^{*}+2\sqrt{a_l})(R_l-2\sqrt{a_l})}\right|+\\&+\left[\frac{2(B_l-a_lF_l)}{3a_l^{3/2}}p^3\frac{2B_lp}{a_l^{3/2}}+\frac{(a_lF_l+B_l)}{a_l^{5/2}}\xi^2p\right]\\&\times\ln\left|\frac{(R_l^{**}-2\sqrt{a_lp})(R_l+2\sqrt{a_lp})}{(R_l^{**}+2\sqrt{a_lp})(R_l-2\sqrt{a_lp})}\right|\\&+\frac{2(a_lF_l-2B_l)}{a_l^2}\left[(1+p^2)(\xi-R_l)+(1-p^2)(R_l^{*}-R_l^{**})\right]\Bigg\}\end{aligned}$$

where $R_l^2=4a_l(1+p^2)+\zeta^2$, $R_l^{*2}=4a_l+\zeta^2$, $R_l^{**2}=4a_lp^2+\zeta^2$, $\zeta=z/h$, $S=4dh$ is the loop area and $p=d/h$ denotes the parameter characterizing the degree of contour 'unequiaxiality'. The factors a_l, B_l, F_l $(l=1,2,3)$ are the combinations of elastic constants c_{ij} $(i,j=1,2,3,\dots 6)$ associated with transversely isotropic medium that can be written as

$$B_l=[(c_{44}-a_lc_{11})(c_{33}-a_lc_{44})+a_l(c_{13}+c_{44})^2]/E_l;$$

$$F_l=[c_{33}(c_{66}-c_{11})+a_lc_{66}(2c_{13}+a_lc_{11})+c_{13}^2]/E_l;$$

$$E_1=4\pi(a_1-a_2)(a_3-a_1);\ E_2=4\pi(a_2-a_3)(a_1-a_2);$$

$$E_3=4\pi(a_3-a_1)(a_2-a_3);\ a_1=c_{44}/c_{66};$$

$$a_{2,3}=\{(c_{11}c_{33}-2c_{13}c_{44}-c_{13}^2)\pm[(c_{13}^2+2c_{13}c_{44}-c_{11}c_{33})^2-4c_{11}c_{33}c_{44}^2]^{1/2}\}/2c_{11}c_{44}$$

The self elastic energy W_{s}^{t} associated with the rectangular twist loop situated in the isotropic plane can be found from an integral expression[26] similar to equation (A1). Calculations show that this energy is equal to

$$
\begin{aligned}
W_s^t = \frac{c_{44}\omega_t^2}{4c_{11}c_{66}}\left(\frac{S}{p}\right)^{3/2} \sum_{l=1}^{3} \Bigg\{ & \frac{2(2B_l - a_l F_l)}{a_l^{3/2}} p(1+p) \\
& + \frac{2(5a_l F_l - 8B_l)}{9a_l^{3/2}} \left[(1+p^2)^{3/2} - 1 - p^3\right] \\
& + a_l^{-3/2} \left[\frac{(a_l F_l - B_l)}{3} - p^2 B_l\right] \Bigg[2\ln\left(\frac{2\sqrt{S}}{r_t}\right) - \ln p \\
& + \ln\left(\frac{\sqrt{1+p^2} - 1}{\sqrt{1+p^2} + 1}\right)\Bigg] \\
& + \frac{p}{a_l^{3/2}} \left[\frac{(a_l F_l - B_l)}{3} p^2 - B_l\right] \Bigg[2\ln\left(\frac{2\sqrt{S}}{r_t}\right) \\
& + \ln p + \ln\left(\frac{\sqrt{1+p^2} - p}{\sqrt{1+p^2} + p}\right)\Bigg]\Bigg\}
\end{aligned}
\tag{A3}
$$

where ω_t is the loop strength and $2r_t$ denotes the disclination core size measured in the isotropic plane. It should be noted that equations (A2) and (A3) have been derived in the approximation $\omega_t^{(1)}, \omega_t^{(2)}, \omega_t \ll 1$ of the linear elasticity theory.

Numerical values of the twist loop energies W_s^t and W_{int}^t in polyethylene were determined by using theoretical elastic constants c_{ij} of an orthorhombic polyethylene crystal given in ref. 15. The values of these constants were preliminarily averaged in accordance with the transversely isotropic model thus neglecting weak elastic anisotropy of polyethylene crystals in the crystallographic planes perpendicular to chain axes. The sizes $2d$ and $2h$ of a rectangular disclination loop were taken to be equal to the dimensions of macromolecule effective cross-section in a polyethylene crystal. The latter were calculated from the geometric parameters of the unit cell listed in ref. 7. The values obtained, $2d = 5.2$ Å, $2h = 3.5$ Å, indicate marked unequiaxiality of disclination loops in polyethylene: $p = d/h \approx 1.5$.